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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Coldwater-Dispersible Compositions of Fat-Soluble Active Substances

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(54) Bezeichnung: KALTWASSERDISPERGIERBARE ZUBEREITUNGEN FETTLÖSLICHER WIRKSTOFFE

(57) Abstract

Partially decomposed soy protein is used as protecting colloid for fat-soluble active substances.

(57) Zusammenfassung

Verwendung von teilabgebautem Sojaprotein als Schutzkolloid für fettlösliche Wirkstoffe.

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Coldwater-dispersible compositions of fat-soluble active substances

The present invention relates to the use of partially degraded soybean proteins as protective colloids for fat-soluble active substances.

The invention further relates to compositions containing fat-soluble active substances and partially degraded soybean proteins and to the use of such compositions.

Fat-soluble active substances such as vitamins and carotenoids play an important part in human and animal nutrition, whether as essential substances such as the vitamins or proteins, or else, specifically in the case of carotenoids, as natural or nature-identical colorants which confer a characteristic color on many human or animal foodstuffs.

It is common to these fat-soluble active substances that in their pure form they can be handled only with difficulty, if at all, because they are oxidation-sensitive substances. Furthermore, a fine dispersion of the active substance is advantageous for optimal absorbability or coloring action. In addition, it is often desirable for the active substances to be dispersible in water. This is why these substances are frequently supplied in the form of emulsions or dry powders, in which case the active substances are embedded, either in pure form or as solution in a physiologically tolerated oil, finely dispersed in a protective colloid.

The sensitivity of oil-soluble vitamins and carotenoids to oxygen makes great demands on the matrix in which the substances are embedded. The protective colloid envelope must, in order effectively to prevent oxidative decomposition processes, represent a good barrier to oxygen. This is why gelatin is frequently used, having excellent stabilizing properties.

According to EP-A 0 347 761, fish gelatin is also suitable as protective colloid for fat-soluble substances.

However, the disadvantage of gelatins is that they have strong adhesive properties. On use of gelatin-containing products the drying methods conventional for liquid systems, such as spray drying or spray fluidized bed drying, may lead to stringing or caking.

In other protective colloids which are frequently used, such as gum arabic, starch, dextrins, pectin or tragacanth, it is often possible to embed only relatively low concentrations of fat-soluble substances. Furthermore, in the past as a consequence of failed harvests, gum arabic in particular has not always been available or available in adequate quality.

Synthetic colloids such as polyvinylpyrrolidone or partially synthetic polymers such as cellulose derivatives likewise have a limited emulsifying capacity and are not always acceptable, especially in the foodstuffs sector.

It is furthermore known to use natural vegetable proteins such as soybean proteins as protective colloids for fat-soluble substances. However, products of this type likewise have a number of disadvantages related to the properties typical of proteins. Those which should be particularly mentioned here are: a tendency to flocculate, which is often pronounced, on exposure to heat or in the presence of salts, and not always adequate emulsifying capacity. In addition, the products produced in this way often have inadequate coldwater dispersibility. Furthermore, vegetable proteins may greatly increase the viscosity of liquid water-containing systems, which may restrict the production or processing of such products.

The use of partially hydrolyzed soybean proteins as substitute for protein-based foaming agents in foodstuffs is disclosed in US-A 3 932 672 and US-A 4 015 019. Partially hydrolyzed soybean proteins can also be used for protein supplementation of soft drinks (H.S. Olsen and J. Adler-Nissen, Zeitschrift für Lebensmitteltechnologie und Verfahrenstechnik, 31 (1980) 259-360).

US-A 4 293 574 discloses the production of mayonnaise-like foodstuffs using specific alcohol-denatured and partially hydrolyzed soybean proteins as substitute for eggs.

It is an object of the present invention to find suitable protective colloids for fat-soluble active substances such as vitamins or carotenoids, and compositions thereof.

We have found that this object is achieved, using partially degraded soybean proteins as protective colloid, and compositions of fat-soluble active substances.

The object of the present invention was to find suitable protective colloids for fat-soluble active substances which do not involve technical disadvantages for processing and make it

possible to produce in a simple way stable, coldwater-dispersible compositions of fat-soluble active substances.

Used according to the invention as protective colloids for fat-soluble active substances are partially degraded soybean proteins which preferably have a degree of degradation ("DH": "degree of hydrolysis") of 0.1 to 5%, particularly preferably 0.2 to 3%. The degree of degradation "DH" is defined as follows:

$$DH = \frac{\text{Number of cleaved peptide linkages}}{\text{Total number of peptide linkages}} \times 100\%$$

The degree of degradation can be determined by the pH-stat method as described by C.F. Jacobsen et al. in Methods of Biochemical Analysis, Vol. IV, pp. 171–210, Interscience Publishers Inc., New York 1957.

The partial degradation is, as a rule, carried out enzymatically, suitable enzymes being proteases from plants, microorganisms, fungi or animals. The partial degradation is preferably carried out with the vegetable protease bromelain.

The soybean proteins usually employed are commercial soybean protein isolates and concentrates with protein contents of from 70 to 90% by weight, where the remaining 10 to 30% by weight represent other more or less undefined plant constituents. The soybean protein isolates are incubated with the enzyme in aqueous medium, preferably at from 50 to 70°C and at a pH of from 7 to 9. The suitable protein to enzyme ratio for the desired degree of degradation can be determined in the individual case by laboratory tests which are simple for the skilled worker.

The aqueous soybean protein hydrolysate solutions are, as a rule, produced in such a way that the protein content is from 6 to 10% by weight.

Suitable fat-soluble active substances according to the invention are vitamins A, D, E and K, derivatives thereof such as vitamin A palmitate or vitamin E acetate, as well as carotenoids, for example β-carotene, apocarotenal, ethyl apocarotenoate, canthaxanthin, zeaxanthin, astaxanthin, lycopene, citranaxanthin or mixtures of said substances.

The fat-soluble active substances can be added to the compositions according to the invention either in pure form or as mixture with physiologically tolerated oils such as sesame oil, corn oil, cotton seed oil, soybean oil or peanut oil.

In addition to the fat-soluble active substances and the partially degraded soybean proteins, the compositions according to the invention may also contain conventional auxiliaries, for example sugars and sugar alcohols, starch or starch derivatives, stabilizers such as t-butyl-hydroxytoluene, as well as emulsifiers such as ascorbyl palmitate or lecithin.

The compositions can be produced in a conventional manner by emulsifying the fat-soluble active substances either in pure form or mixed with physiologically tolerated oils or fats in the aqueous phase containing protective colloid. The emulsification can take place with the aid of conventional stirrers, rotor-stator dispersers and other suitable mixers. It is advisable to carry out the emulsification at 40 to 70°C.

The compositions according to the invention can be either liquid or solid, and solid compositions are preferred. Solid compositions can be produced in a simple manner by spray drying or spray fluidized bed drying.

The compositions according to the invention contain the fat-soluble active substances in amounts of from 2 to 40, preferably 10 to 20, % of the total weight of active substance and protective colloid.

The content of active substance in the compositions depends on the particular use and can be adjusted appropriately.

The compositions according to the invention are outstandingly suitable for use in livestock nutrition, as additive to foodstuffs or, because of their good coldwater dispersibility, as addition to drinking water. Carotenoid-containing compositions are furthermore suitable as foodstuff colorants, especially for soft drinks. The compositions may also be added to other foodstuffs, for example baking mixes or blancmange powders.

The compositions are likewise outstandingly suitable for producing products for supplementing foodstuffs with vitamins.

Examples

In the following Examples 1, 2, 4 and 5, commercial soybean protein isolates with a protein content of 85% by weight were used. A concentrate with a protein content of 65% by weight was used in Example 3.

The bromelain which was used is a commercial enzyme (from Merck, 2m-Ansom-U/mg).

The emulsions were each spray dried in a Minor spray dryer from Niro, the tower inlet temperature being 140°C and the tower outlet temperature being 90°C.

The pH was adjusted in each case with 1 M aqueous NaOH.

Example 1

600 ml of water and 45 g of soybean protein isolate were placed in a 2 l beaker and heated to 60°C with stirring. The pH was then adjusted to 9.0, 0.46 g of bromelain was added and the mixture was stirred at 60°C for 30 minutes. The pH was then readjusted to 9.0. The DH was calculated on the basis of the consumption of sodium hydroxide solution to be 5. The mixture was boiled using an immersion heater for 2 minutes, again cooled to 60°C, and the evaporated water was replaced. Then 80 g of glucose syrup (80%) and 5.0 g of ascorbyl palmitate were added and mixed with the mixture by brief agitation with an Ultraturrax (2000 rpm). Then 55 g of vitamin A acetate (stabilized, 2.1 million IU/g) were emulsified in, and the emulsion was treated further with the Ultraturrax (9000 rpm) for 30 minutes, keeping the temperature of the emulsion at from 55°C to 65°C by occasional cooling with a water bath (20°C). The emulsion was then spray dried.

The resulting powder has a vitamin A acetate content of 0.63 million IU/g.

Example 2

As in Example 1, 45 g of soybean protein isolate were partially degraded in 600 ml of water with 0.19 g of bromelain, 80 g of glucose syrup (80%) and 5 g of ascorbyl palmitate were added, and then 60 g of D/L-alpha-tocopherol were emulsified in. The degree of degradation of the soybean protein was determined to be 2.9%. The emulsion was further processed and spray dried as in Example 1.

The powder had a tocopherol content of 33% by weight.

Example 3

300 ml of water and 34 g of soybean protein concentrate (protein content 65%) were placed in a 1 l beaker and heated to 60°C while stirring with a magnetic stirrer. The pH was then adjusted to 8.0, 0.05 g of bromelain was added and the mixture was stirred at 60°C for 30 minutes. The pH was then readjusted to 8.0, the mixture was subsequently boiled for 2 minutes, 90 g of glucose syrup (80%) and 3.5 g of ascorbyl palmitate were added, and brief mixing was carried out with an Ultraturrax (2000 rpm). The degree of degradation of the protein was 1.6%.

27 g of a 30% by weight dispersion of ethyl apo-8'-carotenoate in a medium chain-length triglyceride ("Miglyol-810") in a 100 ml round-bottom flask were stabilized with tocopherol and dissolved by stirring with a paddle stirrer in an oil bath at 180°C. The hot oily solution was emulsified in the aqueous phase and dispersed with the Ultraturrax at 9000 rpm for 20 minutes, keeping the temperature of the emulsion at about 60°C by cooling with an ice bath. The emulsion was dried in a spray dryer.

The ethyl apo-8'-carotenoate content in the dry powder was 5%.

Example 4

As in Example 1, 20 g of soybean protein isolate were partially degraded in 280 ml of water in a 1 l beaker with 0.002 g of bromelain, 110 g of glucose syrup (80%) and 2.6 g of ascorbyl palmitate were added, and brief mixing was carried out with an Ultraturrax (2000 rpm). The degree of degradation of the protein was 0.1%.

21.7 g of a 20% strength dispersion of citranaxanthin in a medium chain-length triglyceride ("Miglyol 810") in a 100 ml round-bottom flask were stabilized with tocopherol and dissolved by stirring at 180°C. The hot oily solution was emulsified in the aqueous phase and dispersed with the Ultraturrax at 9000 rpm for 20 minutes, keeping the temperature of the emulsion at about 60°C by cooling with an ice bath.

The citranaxanthin content in the dry powder was 3.0%.

Example 5

As in Example 1, 20 g of soybean protein isolate were partially degraded in 280 ml of water in a 1 l beaker with 0.05 g of bromelain. The degree of degradation was 2.2%. After addition of 110 g of glucose syrup (80%) and 2.6 g of ascorbyl palmitate, the mixture was briefly mixed with an Ultraturrax (2000 rpm).

21.6 g of a 20% strength dispersion of β-carotene in peanut oil in a 100 ml round-bottom flask were stabilized with tocopherol and dissolved by stirring with a paddle stirrer in an oil bath at 180°C. The hot oily solution was cautiously emulsified in the aqueous phase and dispersed with the Ultraturrax at 9000 rpm for 20 minutes, keeping the temperature of the emulsion at about 60°C by cooling with an ice bath. The emulsion was dried in a spray dryer.

The β-carotene content in the dry powder was 2.9%.

Orangeade beverages and multivitamin syrups produced with a β-carotene-containing composition according to the invention had a brighter color and greater clarity than those produced using gelatin or natural soybean protein.

We claim:

1. The use of partially degraded soybean proteins as protective colloids for fat-soluble active substances.

2. The use as claimed in claim 1, wherein the partially degraded soybean proteins have a degree of degradation of from 0.1 to 5%.

3. A coldwater-dispersible composition containing fat-soluble active substances as essential ingredients and partially degraded soybean proteins as protective colloid.

4. A composition as claimed in claim 3, which is in solid form.

5. A composition as claimed in claim 3 or 4, containing as fat-soluble active substances vitamins A, D, E or K or a carotenoid or mixtures of these active substances.

6. A composition as claimed in any of claims 3 to 5, containing from 2 to 40% by weight of a fat-soluble active substance based on the total amount of active substance and protective colloid.

7. The use of the compositions as claimed in any of claims 3 to 6 in livestock nutrition.

8. The use of the compositions as claimed in any of claims 3 to 6 as additives in human foodstuffs.

9. The use of the compositions as claimed in any of claims 3 to 6 for human dietary supplementation.